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Feasibility of a Super High Energy Density Battery of the Li/BrF₃ Electrochemical System

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16. Abstract (Limit: 200 words) Feasibility studies on the practical aspects of developing a lithium/bromine trifluoride battery have been studied. Efforts directed toward identifying materials for porous electrode separators, glasses for insulated electrical feed-throughs, and metals for lid, case and current collector fabrication via electrochemical testing techniques have resulted in a list of materials suitable for these applications. Prototype cells utilizing a spirally wound electrode configuration have been constructed and discharged. The use of lithium salts as an electrolyte additive has been explored, and has shown a positive effect on discharge performance. Through the use of currently available technology, however, the lithium/bromine trifluoride couple has not delivered energy density comparable to other high energy density lithium systems. This investigation has revealed that practical Li/BrF ₃ cell development will require further extensive fundamental electrochemical research.			
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INTRODUCTION

Bromine trifluoride (BrF_3) used in conjunction with lithium offers the possibility of batteries having very high cell voltages and energy densities. Consequently, the feasibility of developing a lithium bromine trifluoride battery has been under investigation [1,2].

The concept of a "Super High Energy Density Battery" of the Li/BrF_3 couple utilizing an antimony pentafluoride (SbF_5) electrolyte had been patented previously by the U.S. Navy [3]. More recently, Miles and coworkers at the Naval Weapons Center (NWC - China Lake, CA) have been reporting on experiments directed towards determining the suitability of BrF_3 as a lithium cell catholyte [5,6]. Miles' results suggest that it may be feasible to develop practical lithium cells of the Li/BrF_3 couple that will have operating voltages above 4.5 V at current densities of 20 mA/cm^2 .

To compliment the current work being done at NWC, Wilson Greatbatch Ltd. (WGL) proposed to perform feasibility studies on the practical aspects of lithium cell design utilizing BrF_3 depolarizer.

Studies focused on the following:

- (1) metals and alloys for battery containment;
- (2) cathode substrate/metal current collector couples;
- (3) hermetic electrical feedthroughs;
- (4) interelectrode separator material;
- (5) internal insulators;
- (6) cathode substrate materials;
- (7) long term lithium anode stability in lithium bromine trifluoride containing either lithium tetrafluoroborate or lithium hexafluoroarsenate salts; and,
- (8) energy density of prototype lithium bromine trifluoride batteries.

This is the final report summarizing test findings related to materials compatibility and performance of prototype Li/BrF_3 cells.

(1) METALS AND ALLOYS FOR BATTERY CONTAINMENT

The corrosion resistance of individual selected metals and alloys in BrF_3 was evaluated by means of immersion storage tests and by potentiodynamic polarization scans. All studies employed as-received BrF_3 obtained from Atochem North America.

(i) BrF_3 IMMERSION TESTING OF SELECTED METALS AND ALLOYS:

Initial compatibility testing involved storage of metal/alloy coupons immersed in BrF_3 . Thirty coupons cut from 10 selected metals/alloys were cleaned, weighed, and placed in individual

conical Teflon PFA vials. Working in a glove bag containing a teflon-lined stainless steel tray, BrF₃ was added to each vial and the vials were capped. Approximately 6 cycles of evacuation and dry argon purge were carried out prior to filling and capping to minimize atmospheric contamination. Storage of the 3 groups of 10 vials was for 2, 30 and 90 days, respectively. Upon removal, each coupon was washed in trichlorotrifluoroethane, reweighed, then examined via scanning electron microscopy (SEM). Surface condition was compared to virgin material.

Technical Report 0001AA presented results for 2 day storage while Progress Report 0001AB listed the 30 day results. The 90 day findings are added in Table I. As previously noted, insignificant poststorage weight changes occurred. Except for 304 L SS and mild steel which exhibited small areas of pitting corrosion, sample condition was comparable to that reported earlier.

TABLE I - Metal Evaluation Results

<u>Sample</u>	<u>Pre/post test</u> <u>Wt. (g) 2 days</u>	<u>Pre/post test</u> <u>Wt. (g) 30 days</u>	<u>Pre/post test</u> <u>Wt. (g) 90 days</u>
Mild Steel	.203/.204	.304/.302	.465/.466
304 L SS	.039/.040	.013/.012	.026/.026
316 L SS	.019/.020	.031/.030	.033/.034
Nickel 200	.293/.293	.408/.407	.361/.361
Superferrit	.087/.087	.133/.133	.158/.158
Shomac	.045/.045	.055/.054	.041/.041
Aluminum 1145-0	.031/.031	.024/.023	.020/.020
Hastelloy G30	.507/.506	.657/.656	.605/.605
29-4-2	.072/.072	.104/.103	.099/.099
Monel 400	.473/.473	.192/.192	.294/.294

(ii) POTENTIODYNAMIC POLARIZATION - SELECTED ALLOYS VERSUS PLATINUM REFERENCE

Potentiodynamic polarization was employed to provide a qualitative means of comparing the behavior of 10 selected metals in BrF₃. Progress Report 0001AB outlined the procedure used. Also included were the polarization plots for Superferrit®, Nickel 200, Aluminum 1145-0, 29-4-2, Shomac®, 316 L SS and Monel 400. Figures 10 through 12 represent the results for 304 L SS, Hastelloy® C22 and lithium.

Table II lists the measured corrosion potential (E_{corr}), corrosion current density (I_{corr}) and the calculated corrosion rate for the metals/alloys evaluated using platinum as the reference electrode. Response comparisons suggest Aluminum 1145-0 most resistant to bromine trifluoride with Nickel 200 and Shomac® as alternates.

TABLE II - Potentiodynamic Polarization Results - Platinum Reference Electrode

<u>Material</u>	<u>E_{corr} (mV)</u>	<u>I_{corr} (μA/cm²)</u>	<u>Corrosion Rate (MPY)</u>
Superferrit®	- 452	.26	.08
Nickel 200	- 68	.07	.02
Shomac®	- 161	.07	.02
316 L SS	- 343	1.46	.39
Monel 400	- 500	1.46	.35
304 L SS	- 287	.90	.24
29-4-2	- 170	1.57	.43
Aluminum	-1021	.08	.01
Hastelloy® C22	- 608	1.27	.32
Lithium	-5143	429.30	725.21

(2) CATHODE SUBSTRATE/METAL CURRENT COLLECTOR COUPLES

The possibility of enhanced corrosion due to galvanic and/or crevice effects exists where metallic current collectors contact carbon composite cathode substrate materials. This was addressed by immersion testing and by normalizing the potentiodynamic polarization scans previously obtained such that data obtained is referenced to lithium.

(i) BrF₃ IMMERSION TESTING OF COUPLES

To study the effect of cathode substrate in contact with current collector material, expanded metal screens were prepared by pressing carbon cathode substrate material onto Nickel 200, 304 L SS and Superferrit screens. Couples were immersed in BrF₃ and stored for 1 and 90 days as in (1i) above. After removal from the vials, couples were separated and the screens were washed in trichlorotrifluoroethane prior to SEM examination and comparison with virgin screens.

Figures 1 through 3 represent virgin screen material. The 1 day storage samples are presented in Figures 4 through 6. Samples stored for 90 days are shown in Figures 7 through 9. Samples stored for 1 day exhibited virtually no difference in surface condition when compared to virgin samples. After 90 days, however, Nickel 200 exhibited some intergranular corrosion, pitting corrosion was observed for the 304 L SS sample, and general corrosion of the Superferrit sample was noted.

(ii) POTENTIODYNAMIC POLARIZATION - METAL/ALLOY SAMPLES VERSUS LITHIUM REFERENCE

Carbon tends to assume highly noble electrode potentials in various electrolytes. Practical lithium cells frequently employ carbon composite substrate material pressed into intimate contact with a metallic current collector. In such couples, the metal may become

anodic relative to the carbon, that is, galvanically enhanced corrosion of the collector is possible. More specifically, in a cell consisting of the lithium anode versus carbon substrate couple immersed in BrF_3 , if the equilibrium potential of the current collector is found to be less noble than that of the carbon substrate, electron flow between collector and carbon can be significant as can the associated corrosion of the collector.

To facilitate comparison of candidate current collector materials, the potentiodynamic measurements of Table II were recalculated with reference to lithium. The lithium corrosion potential versus platinum was determined to be -5143 mV. Relating this value to the metal/alloy corrosion potentials versus platinum (Table II) allowed the desired recalculation yielding the E_{corr} value given in Table III. The current densities (I_{corr}) and corrosion rates of Table III were calculated on the basis of 5000 mV difference versus lithium since the open circuit voltage of carbon cathode substrate versus lithium in BrF_3 was found to average 4900 mV. These data suggest that Nickel 200 may be the best current collector candidate with Shomac[®], aluminum and 29-4-2 as alternates.

TABLE III - Potentiodynamic Polarization Results - Lithium Reference Electrode

<u>Sample</u>	<u>E_{corr} (mV)</u>	<u>I_{corr} ($\mu\text{A}/\text{cm}^2$)</u>	<u>Corrosion Rate (MPY)</u>
Superferrit [®]	4691	.462	.14
Nickel 200	5075	- .291	in cathodic range
Shomac [®]	4982	.355	.09
316 L SS	4800	1.479	.40
Monel 400	4643	.828	.20
304 L SS	4856	1.034	.28
29-4-2	4973	.568	.16
Aluminum	4122	.316	.14
Hastelloy [®] C22	4535	.815	.20

(3) HERMETIC ELECTRICAL FEEDTHROUGHS

Glass and ceramic-to-metal seals offer a means for hermetically sealing lithium batteries. Given that battery performance relies on retention of cell hermeticity, and that retention of cell hermeticity depends on preservation of seal integrity, storage of various sealing glasses/ceramics in PFA conical vials was performed. Progress Report 0001AB summarized macroscopic visual results for Fusite 435, K brown, T clear, TA23, Cabal 12 (etched and as received), TM9 B, 9013 Mansol, 9013 Corning, Fusite A485, Fusite MSG 12, Fusite R1, and alumina. Silicate glasses were observed to exhibit immediate bubble evolution when BrF_3 was introduced. After one month of room temperature storage, these glasses were visibly etched, with some samples disintegrating on handling. SEM examination revealed significant

stress corrosion cracking. Of the glasses tested, Cabal 12, a nonsilica glass, and alumina, a ceramic, proved most promising. Poststorage conditions are shown in Figures 13 through 15.

(4) INTERELECTRODE SEPARATOR MATERIAL

Successful separation of electrode components is crucial to both the performance and safety aspects of lithium cells. Favorable battery separator characteristics include: (1) resistance to degradation in the cell environment, (2) sufficient strength to facilitate cell fabrication, (3) porosity such that electrode separation is maintained while ionic transfer within the electrolyte is unimpeded, (4) surface energy such that electrolyte wettability and absorption are augmented, (5) sufficient thickness to maintain interelectrode separation without impedance to battery high performance, and (6) freedom from contaminants and reactive species capable of adversely affecting cell performance.

Progress Report 0001AB presented initial results for Whatman BSF45, Kaowool 90105-01, Hollingsworth and Vose BG03013 (inorganic) and for Rayperm[®] 200/60 fluoropolymer. Positive results were obtained for Rayperm[®] after 1 storage month in BrF₃. The sample was returned to the PFA vial for 180 day storage.

The Rayperm[®] separator, supplied by Raychem Ltd., is fabricated from Tefzel[®], ethylenetetrafluoroethylene (ETFE). Rayperm[®] exhibits an elliptical pore structure as depicted in Figure 16. Product literature reports effective pore radius of 0.2 microns and 60% total porosity as determined by mercury porosimetry. It is heat sealable, has low surface energy and is not easily wetted by water.

Given the favorable results obtained with Rayperm[®], additional compatibility testing was initiated. In addition to the original storage sample, two groups of twelve samples were prepared from stock 1.75 inch wide by .002 inch thick material. Group 1 comprised samples cut 1" X 7" in the material machine direction (MD) while group 2 samples, 1" X 1.75", were cut in the material transverse direction (TD). Three samples from each group were stored at room temperature for 1 day, 2 weeks and 1 month immersed in BrF₃ with 3 virgin samples serving as control. A capped 2" high X 1" diameter PFA vial served as the storage vessel.

To evaluate sample degradation, material tensile properties before and after BrF₃ storage were determined using an Instron Model 1130 Universal Tensile Machine. Samples were removed from the storage vials then rinsed 3 times in trichlorofluoroethane. After a final rinse in a 3:1 solution of ethyl alcohol and water followed by air drying, ultimate tensile strength (UTS) and elongation to failure (%E) were determined at a crosshead speed of 1.0 inch per minute. Gage length was 5 inches in the MD and 1 inch in the TD.

TABLE IV - Tensile Test Results for Room Temperature Storage of Tefzel® in BrF₃

<u>SAMPLE</u>	<u>TD/UTS</u>	<u>MD/UTS</u>	<u>TD/%E</u>	<u>MD/%E</u>
Virgin1	1.21	7.04	21.9	359.4
Virgin2	1.32	6.60	28.1	281.3
Virgin3	1.21	8.36	25.0	421.9
1 Day1	1.21	7.48	27.5	406.3
1 Day2	1.10	6.38	25.0	312.5
1 Day3	1.10	6.60	25.0	359.4
2 Wks1	1.21	7.04	21.9	359.4
2 Wks2	1.21	7.48	21.9	390.6
2 Wks3	1.10	6.16	21.9	312.5
1 Mo1	1.21	6.16	28.1	281.3
1 Mo2	1.21	4.84	25.0	250.0
1 Mo3	1.21	7.04	21.9	343.8

Degradation of the test samples was not apparent. Upon removal from the storage vial, all were found to be fully intact with no evidence of embrittlement. Table IV summarizes the tensile test results. Figures 17 through 19 display poststorage surface condition. Figure 20 represents the original specimen after 180 day storage. Comparison with Figure 16 shows little, if any, change.

Porosimetry via Coulter Porometer was performed on the virgin and 30 day storage specimens. Results were as follows:

	<u>Virgin</u>	<u>30 Days</u>
Minimum pore size (μm):	.065	.065
Maximum pore size (μm):	.180	.192
Mean pore size (μm):	.096	.111
Bubble point (μm):	.184	.195

Although the sample size was small, the data obtained suggests that, at room temperature, degradation of Tefzel® in BrF₃ is not imminent; this material may be viable for use as separator for a Li/BrF₃ cell.

(5) INTERNAL INSULATOR MATERIALS

In addition to the interelectrode separator, practical battery design incorporates other internal insulator components. Bromine trifluoride is known to react violently with many organic compounds. The literature suggests the following organics compatible with BrF₃: polytetrafluoroethylene (PTFE), polyfluoroethylenepropene (FEP), and polyperfluoroalkoxyethylene (PFA) [4]. These along with polyethylenetetrafluoroethylene (Tefzel) and polyethylenechlorotrifluoroethylene (Halar) were evaluated for long term stability in BrF₃ by immersion storage tests. Ten coupons were

cut, cleaned, sized, weighed, and placed in individual conical Teflon PFA vials. The vials were capped and stored for 90 days. Upon removal, each coupon was washed in trichlorofluoroethane, reweighed, then examined via scanning electron microscopy (SEM). Sample condition was compared to virgin material.

All coupon weights, sizes and configurations remained unchanged when compared to prestorage conditions. SEM examination revealed no evidence of crazing or stress corrosion cracking. Elastomeric properties appeared unaffected by storage.

(6) CATHODE SUBSTRATE MATERIALS

Desirable attributes for high performance cathode substrate materials include high cell voltage, high energy density capability, good conductivity and compatibility with the battery electrolyte. Two candidate substrate materials were studied: (1) a carbon-teflon powder mixture, and (2) carbon monofluoride. Coupons, 1/2 inch diameter by 1/8 inch thick, were stored in BrF_3 for 90 days. Upon removal from the storage vial, coupons remained intact with no evidence of dissolution or embrittlement.

(7) LONG TERM LITHIUM ANODE STABILITY

Because lithium is strongly electropositive leading to high voltages when coupled with suitable cathode materials and has high gravimetric and volumetric specific capacity, it is a highly desirable anode material. Lithium, however, forms a highly protective passive film in BrF_3 , as it must in any cell having useful shelf life. Such film may be composed of a dense, very thin inner layer topped by a thicker, more porous outer layer. If the passive layer formed in a given electrolyte becomes excessively protective, severe voltage delays may be observed.

For the initial assessment of lithium stability in BrF_3 , a 1.000" X .250" X .011" coupon was stored in BrF_3 for 90 days. Immediately upon immersion, a gray film formed on the lithium. After 90 days storage, the intensity of the gray film remained unchanged. Figure 21 depicts an SEM photograph of the lithium surface after 90 days storage. Film formation appeared uniform with an apparent thickness of approximately .001 inch. To determine the effect of film formation on cell performance, additional study is required.

(8) PROTOTYPE BATTERY ENERGY DENSITY

Test Cell Construction:

A spirally wound 1/2 AA configuration was chosen as the test vehicle for initial prototype cell development efforts. Dimensional data and a description of the components used in the cells are provided in Figure 22. The cathodes consisted of a high surface area carbon cathode formed by compression of a dry carbon black/PTFE[®] mixture

onto an expanded Superferrit[®] grid. A tab of similar material was resistance spotwelded to the current collector grid to act as the cathode lead. The electrochemical surface area of this design was determined to be 14.5 cm².

The anode was comprised of a section of pure lithium metal into which a tab of Superferrit[®] stock was pressed. The single piece of tab stock served as the current collector and external lead. Electrical insulation of the electrodes was accomplished through the use of a two layer separator arrangement. A microporous Tefzel[®] (ETFE) film was located adjacent to the carbon cathode to provide a positive barrier to dislodged carbon particles. The second layer was made up of a woven Tefzel[®] cloth which imparted a high degree of mechanical strength to the separator assembly and was located facing the anode. In addition to being tear resistant the compatible surface energy of the ETFE fibers allowed the bromine trifluoride catholyte to be readily absorbed and transported into the inter-electrode gap.

After the spirally wound electrode stack was inserted into the cell case, a two layer disk of the woven Tefzel[®] was positioned above the stack. This disk served as a diffuser plate to prevent the electrolyte stream from dislodging carbon during the filling operation.

The cell case consisted of a Teflon[®] (PFA) round bottomed test tube 2.50" long with an outside diameter of 0.625" and a wall thickness of 0.030". After insertion of the internal components, the Superferrit[®] electrode leads were directed against the internal cell wall and fixed in place by insertion of the tapered header assembly. The header, which provided the gas tight seal for the cell, consisted of a tapered Teflon[®] (PTFE) stopper into which had been inserted two 0.125" O.D. PFA tubes used for introduction of catholyte into the cell.

Equipment used for filling the cells is diagramed in Figure 23. Following assembly and closure of the test cell in a dry atmosphere it was placed behind a Lexan[®] safety shield and the pressure transfer tube was connected to the 3-way valve. The filling/vent tube was inserted into the electrolyte reservoir to which is added the electrolyte solution. The 3-way valve is opened allow a flow of high purity argon to pass through the cell and through the solution thus removing any volatile impurities caused by hydrolysis reactions. After the electrical connections had been made between the measuring equipment and the electrode leads, the valve is rotated to connect the pre-evacuated low pressure reservoir with the test cell. The contents of the electrolyte reservoir are then drawn into the test cell. The valve is finally positioned to allow a slow stream of argon to sweep through the cell. This arrangement prevents a pressure build-up of reaction off-gasses to occur within the cell while maintaining an inert internal environment. Secondary safety shielding is then put in place and the cells electrochemical performance is evaluated.

The BrF_3 depolarizer solutions employed were straight BrF_3 (Atochem North America) used as received, or BrF_3 mixed (stirred for at least 1 hour and the solution decanted from the insolubles) with either LiBF_4 (Morita - Japan) or LiAsF_6 (Lithco Lectro-Salt). These salts were dried overnight in vacuum at 120°C before use. The solutions were prepared by stirring approximately 0.3 g of each salt with 10 to 15 g of BrF_3 under an argon stream. Slight effervescence accompanied this process for both salts and was observed to taper off, but not cease, over about 2 hours time. The effervescence was more pronounced with the LiBF_4 solutions than with the LiAsF_6 solutions. Although the actual solubility of these salts was never determined, in all cases it was estimated that a solution of less than 1% by weight of the solute was formed. A possible explanation for the effervescence could be the evolution of BF_3 or AsF_5 gas to form $\text{Li}^+ + \text{BrF}_4^-$ in-situ with the reaction proceeding more rapidly in the case of LiBF_4 . A literature search could produce no record of a material of this composition being isolated previously, and we offer this hypothesis as a possibility without confirmation at this time. The only evidence for any reaction or dissolution we have is that there was a positive effect on the test cell discharge results.

Test Results:

Six test cells of the 1/2AA size were successfully discharged through constant resistive loads of either 20Ω (3 - one each of straight BrF_3 , $\text{LiBF}_4/\text{BrF}_3$, $\text{LiAsF}_6/\text{BrF}_3$) or 250Ω (3 - same). Figures 24 - 27 display the discharge curves for these test cells. Under 20Ω load (Figures 24 and 25) the discharge voltage sloped down rapidly over a time-frame of up to one hour. All of the test cells fell below 3 volts within 2 minutes of the initiation of discharge with the straight BrF_3 test cell falling off the fastest. At 3 volts a 20Ω load corresponds to a discharge current density of approximately 10 mA/cm^2 . At this rate, the highest capacity achieved was with either of the lithium salts (LiBF_4 or LiAsF_6) being employed. Figure 25 shows that the capacity to 2 V was approximately 13 to 15 mAh with the salts, and approximately 4 mAh without.

Under the less stressful 250Ω load the cells containing a lithium salt additive maintained a voltage above 4 V from 80 minutes to 160 minutes. At 4.5 V a 250Ω load corresponds to a current density of 1.2 mA/cm^2 . Without the salt the cell could only manage a voltage slightly above 2 V (this test was repeated with similar results). The capacity achieved to a 4 V cutoff was 45 - 50 mAh with the LiBF_4 salt and approximately 25 mAh with LiAsF_6 additive. To a 2 V cutoff the corresponding capacities were 65 and 30 mAh respectively. This would suggest a surprisingly low energy density estimate of only 0.065 Wh/cm^3 for 1/2 AA size cells of the Li/ BrF_3 couple with lithium electrolyte salt added - over an order of magnitude lower than is commonly realized in Li/oxyhalide cells of similar size.

Melvin H. Miles and coworkers of the NWC, have reported test cell results [5,6] using laboratory test cells which utilized 1-2 cm² Li disk anodes immersed in straight BrF₃ (and also BrF₃ containing NaF electrolyte salt), a carbon cathode disk, and a 3 cm diameter cylindrical platinum screen as reference electrode. These test cells were discharged using constant current at rates corresponding to from 5 to 50 mA/cm². At 5 mA/cm² they achieved a normalized capacity of approximately 18 mAh/cm². Our cells (with LiBF₄ additive) discharged at 1.2 mA/cm² and normalized in this way would achieve a value of only 3 mAh/cm². There were many differences in the details of the NWC test cells and the WGL test cells. It is not known what part these differences played in the discrepancies, although it is worth mentioning that the NWC test cells were of the button style and utilized stainless steel springs for electrode contact perhaps helping to keep a tight interfacial separation between anode and cathode. The WGL cells were of the cylindrical wound element type, and the winds were relatively loose (compared with normal product) for safety reasons. The NWC group has also suggested that the main failure mode for the Li/BrF₃ cells is the severe passivation of the lithium surface while in contact with the BrF₃ depolarizer.

One final comment from a safety standpoint. It should come as no surprise given the reactive nature of the BrF₃ material that there were some anxious moments in the laboratory. Of 10 test cell experiments, 2 ended abruptly in explosions. These explosions both occurred within seconds of filling the test cells. One of the explosions was preceded by a notable flash near the top of the cell stack (visible due to the transparent PFA tubes used as cases). The other explosion occurred with no visible precursor. Both explosions occurred within 1 to 3 feet of the investigators. There were no injuries, nor extensive damage as a result of these incidents. The authors believe that the lack of injury or major damage was due to two main factors: (i) excellent shielding, and (ii) the nonmetal cases (tubes) being employed for cell containment. After the two incidents the experiments were changed slightly by incorporating a porous teflon diffuser plate at the top of the cell stack to prevent the rush of liquid BrF₃ during filling from breaking off chunks of the carbon cathode, and by fabricating the anodes just prior to the experiment (not a day or two ahead of time) because of a concern about lithium nitride (Li₃N) formation in the anode during the waiting period. It is not known for certain what effect these changes had on the safety of the test cells, but there were no additional safety incidents for the remaining seven consecutive test cell experiments.

CONCLUSIONS

The results obtained during this Phase I effort lead to the following conclusions:

1. It is feasible to conduct Li/BrF₃ primary cell research on

spirally wound element cell configurations.

2. There are suitable materials available for Li/BrF₃ cell construction. Among these are...

- a) cell separators - fluoropolymer films or woven fabrics, binderless nonsilica containing glass (or ceramic) fiber paper,
- b) containers - fluoro polymers, nickel, aluminum, corrosion resistant ferritic stainless steels,
- c) electrode current collectors - same metals as in "b,"
- d) insulators - same as in "a,"
- e) hermetic insulating feedthrough - nonsilica containing glasses or ceramics.

3. The use of suitable lithium salts such as LiBF₄ and LiAsF₆ improves the discharge characteristics of Li/BrF₃ cells.

4. Using current technology, the Li/BrF₃ couple has not delivered energy density comparable to other high energy density lithium systems.

RECOMMENDATIONS

1. Practical Li/BrF₃ cell development will require further extensive fundamental electrochemical cell research. This is mostly because of the extreme reactivity of the BrF₃ material and the need to maintain a safe experimental environment for cell fabrication and testing - this in excess of what is normally required of more common lithium cell research and development.

2. Additional research is required on the solubility and conductivity of electrolyte salts in BrF₃, and their effects on cell discharge performance.

3. More research is required on the effects and methods of purifying the BrF₃.

4. Further investigation on the actual failure mode of Li/BrF₃ cells is required.

5. Development of rugged and practical cell designs will be necessary.

6. The question of the feasibility of a primary "active" Li/BrF₃ cell has not been satisfactorily resolved. Consideration of reserve type prototype development needs to be addressed.

7. The possibility of depolarizer mixtures including BrF₃ as either a major or minor constituent should be investigated.

8. Alternate cathode substrate materials other than straight carbon or mixtures with carbon should be tried.

REFERENCES:

1. Pyszczyk, M.F., Ebel, S.J., Frysz, C.A., "Feasibility of a Super High Energy Density Battery of the Li/BrF₃ Electrochemical System," Technical Report 0001AA, Wilson Greatbatch Ltd, Clarence, NY, (1989).
2. Pyszczyk, M.F., Ebel, S.J., Frysz, C.A., "Feasibility of a Super High Energy Density Battery of the Li/BrF₃ Electrochemical System," Progress Report 0001AB, Wilson Greatbatch Ltd, Clarence, NY, (15 December 1989).
3. Goodsen, F.R., Shipman, W.H., McCartney, J.F., U.S. patent number 4,107,401, 1978.
4. Boyd, W.K., Berry, W.E., White, E.L., "Compatibility of Materials with Rocket Propellants and Oxidizers," NASA Accession No. N65-24361, AD 613553, report UNCLASSIFIED, January 20, 1965.
5. Park, K.H., Miles, M.H., Bliss, D.E., Stilwell, D., Hollins, R.A., Rhein, R.A., *J. Electrochem. Soc.*, 135, 2901, 1988.
6. Park, K.H., Stilwell, D.E., Bliss, D.E., Hollins, R.A., Miles, M.H., "A Comparison of Lithium, Magnesium and Calcium Anodes in Bromine Trifluoride," *Electrochem. Soc. Extended Abstracts*, 88-2, 30, 1988.

APPENDIX:



FIGURE 1: Virgin Nickel 200 expanded metal screen. ~600X

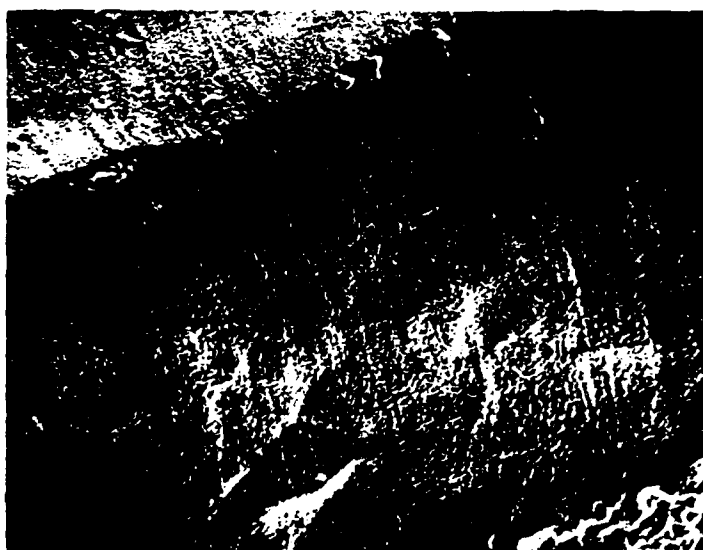


FIGURE 2: Virgin Superferrit® expanded metal screen. ~600X



FIGURE 3: Virgin 304 L SS expanded metal screen. ~600X

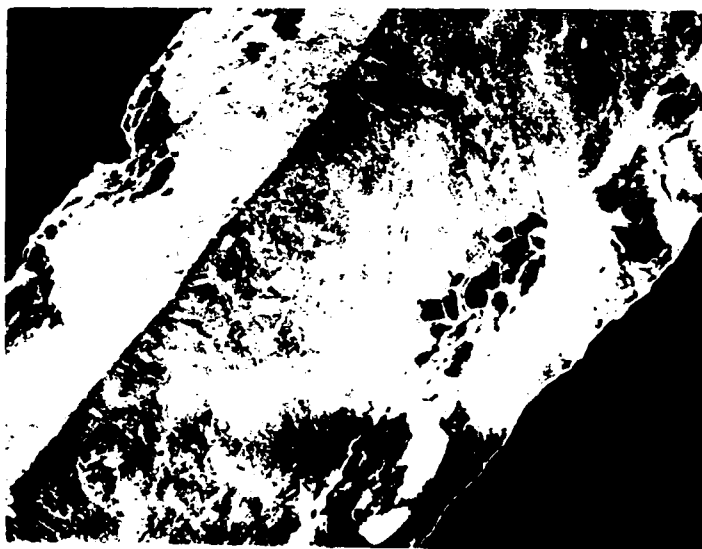


FIGURE 4: Nickel 200 expanded metal screen after 1 day storage in BrF_3 . 600X

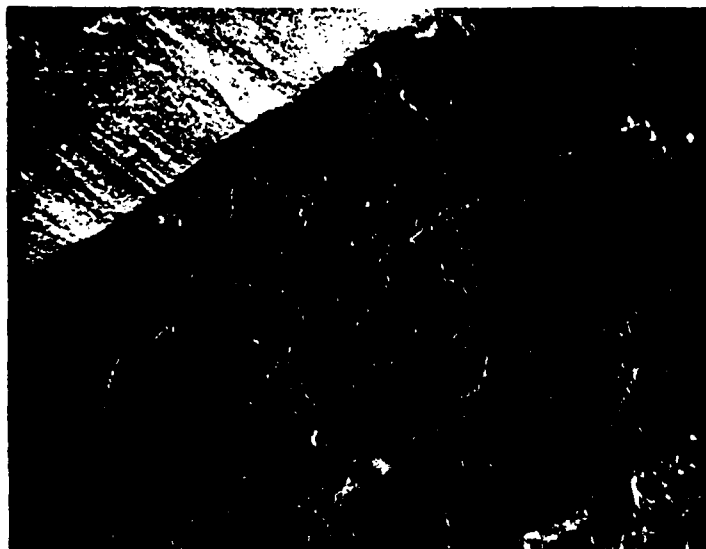


FIGURE 5: Superferrit[®] expanded metal screen after 1 day storage in BrF_3 . ~600X.

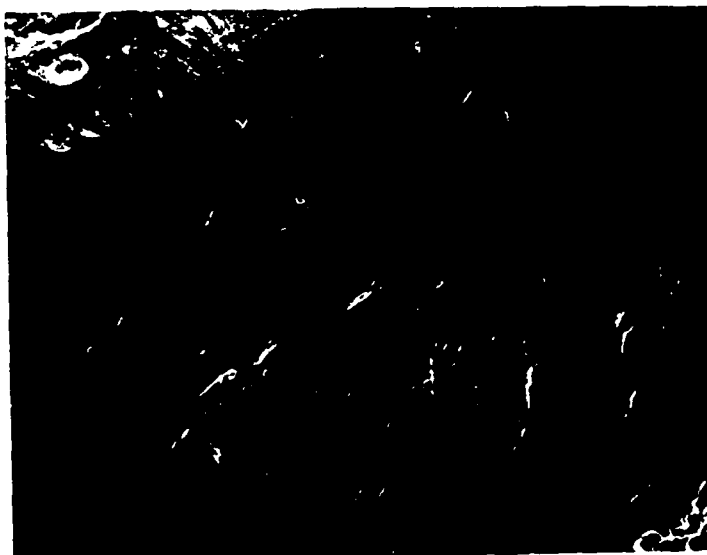


FIGURE 6: 304 L SS expanded metal screen after 1 day storage in BrF_3 . ~600X

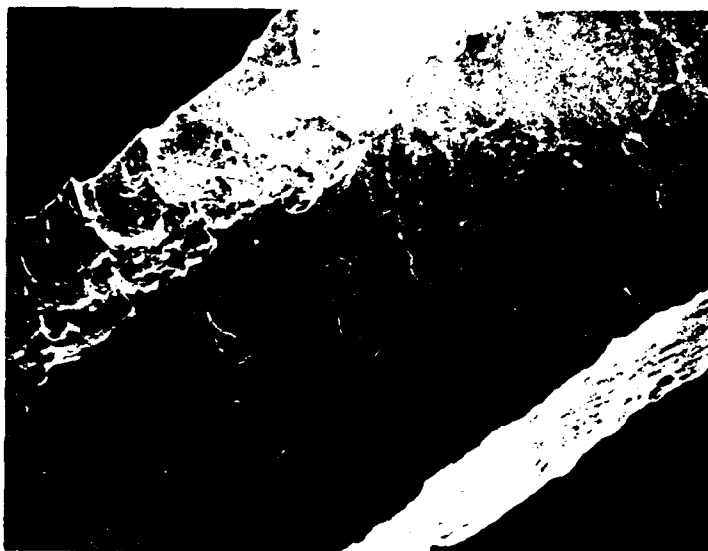


FIGURE 7: Nickel 200 expanded metal screen after 90 days storage in BrF_3 . 600X

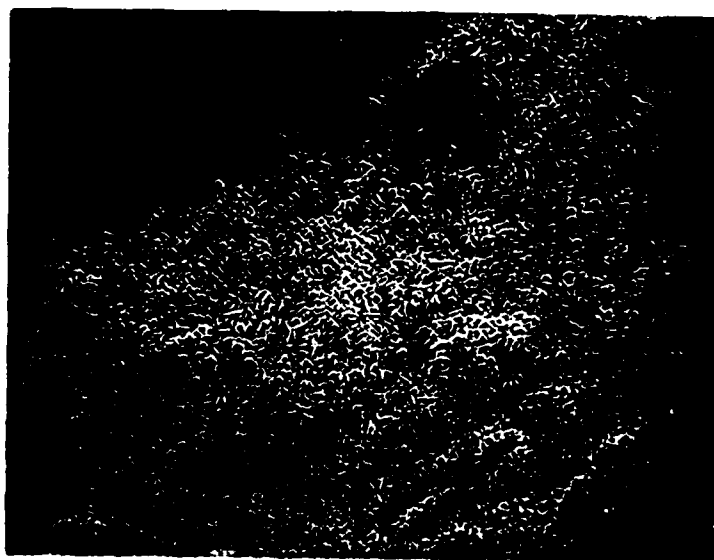


FIGURE 8: Superferrit[®] expanded metal screen after 90 days storage in BrF_3 . ~600X



FIGURE 9: 304 L SS expanded metal screen after 90 days storage in BrF_3 . ~600X

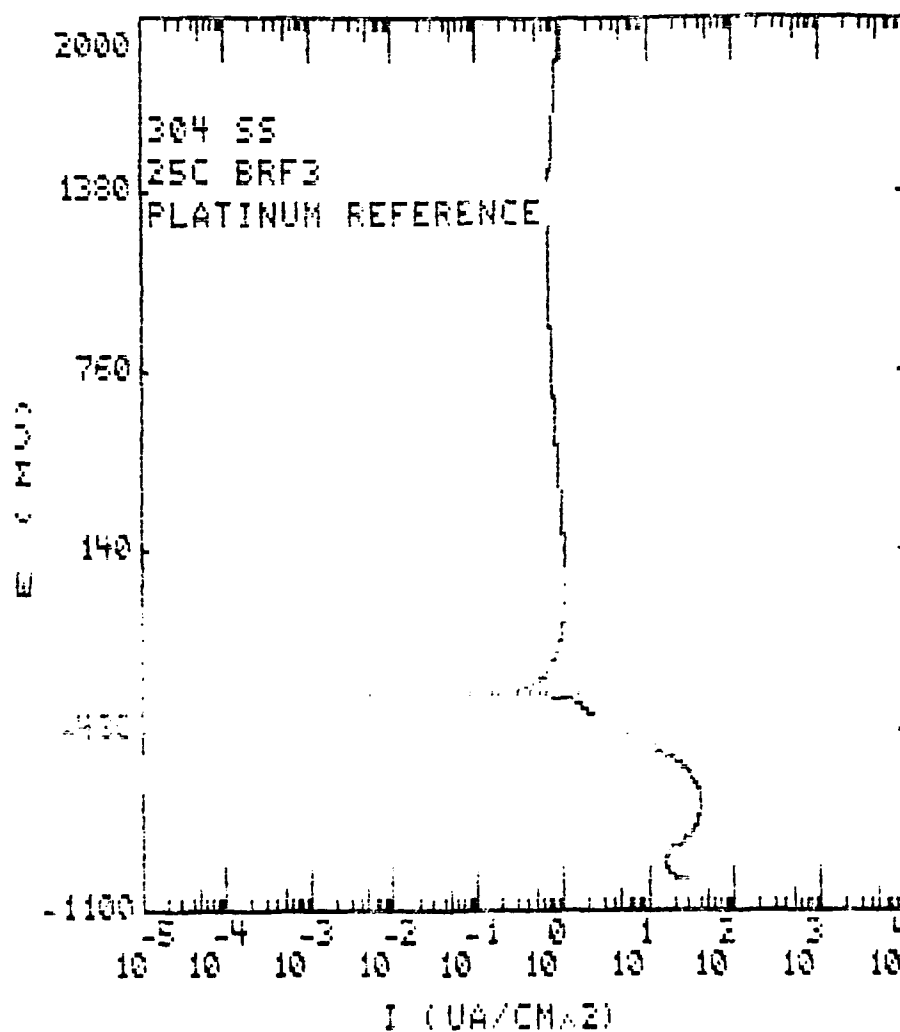


FIGURE 10: Potentiodynamic polarization plot for 304 L SS in BrF_3 . (Platinum reference electrode)

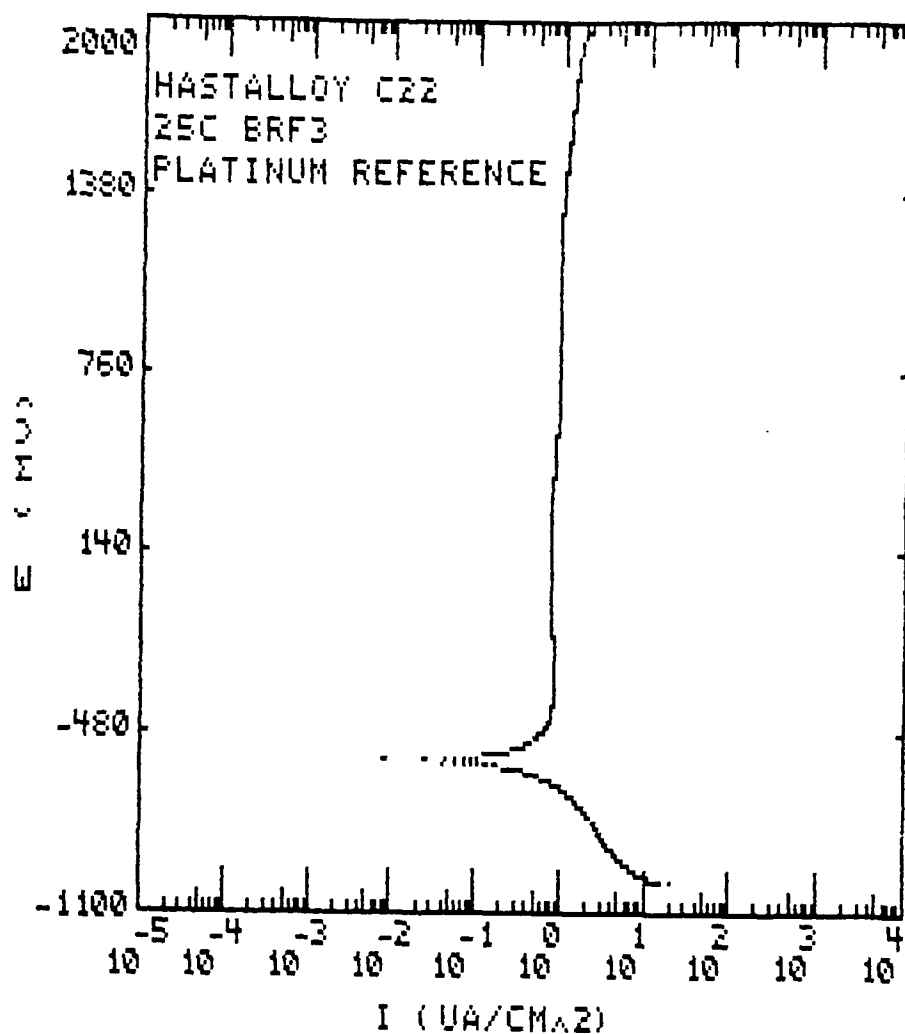


FIGURE 11: Potentiodynamic polarization plot for Hastelloy® C22 in BrF₃. (Platinum reference electrode)

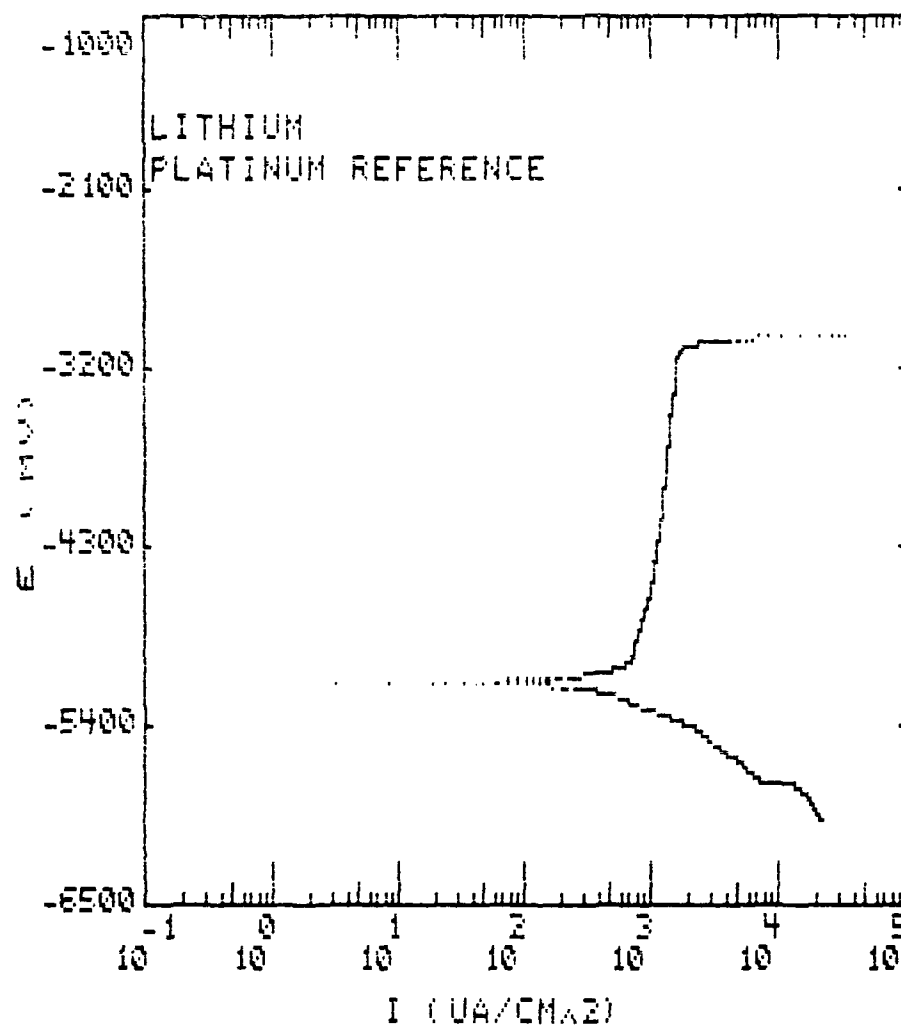


FIGURE 12: Potentiodynamic polarization plot for lithium in BrF₃.
(Platinum reference electrode)

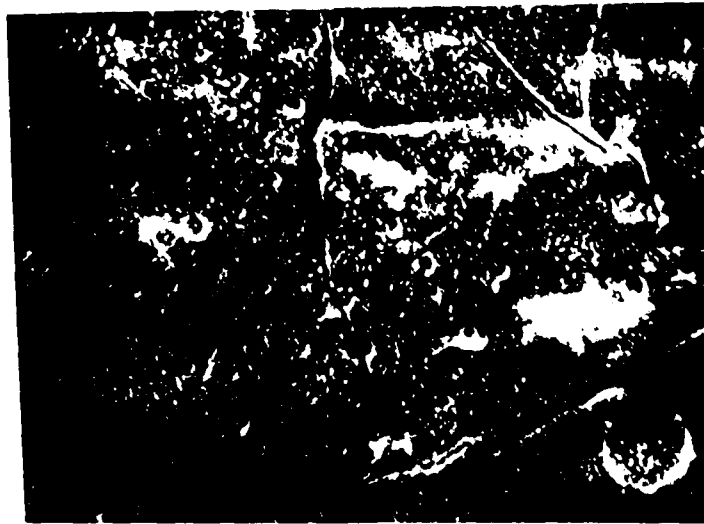


FIGURE 13: Typical poststorage silicate glass surface. ~600X

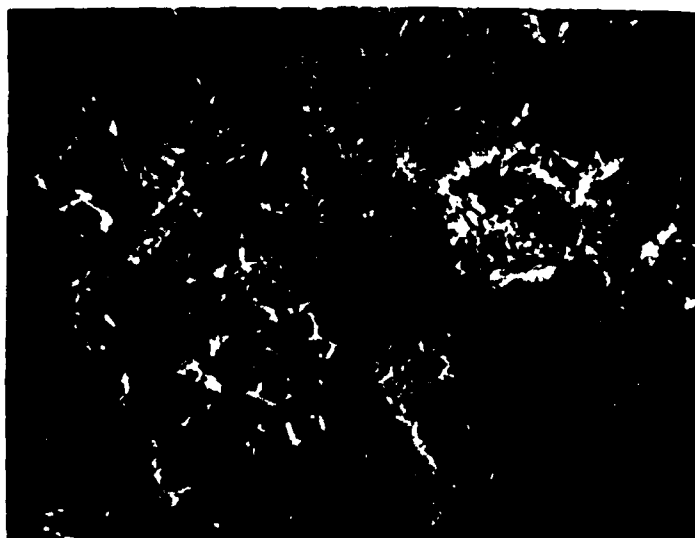


FIGURE 14: Poststorage Cabal 12 glass surface. 600X

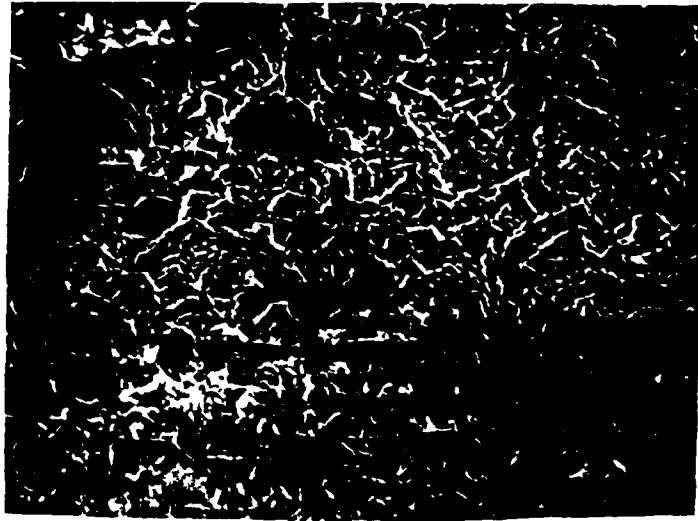


FIGURE 15: Poststorage alumina surface. ~600X

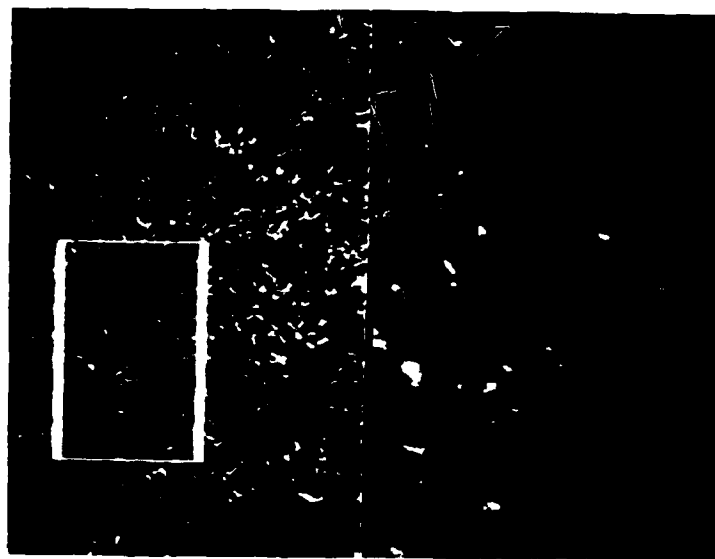


FIGURE 16: Virgin Rayperm[®] pore structure. 600/1800X

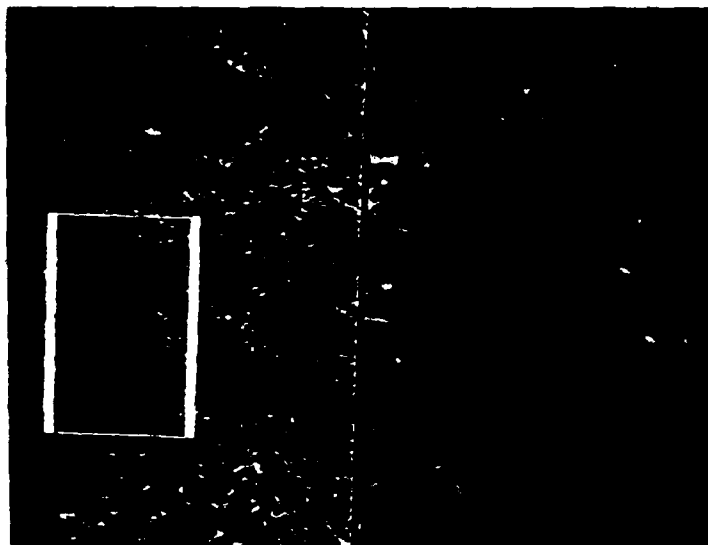


FIGURE 17: Rayperm[®] pore structure after 1 day storage in BrF₃.
~600/1800X

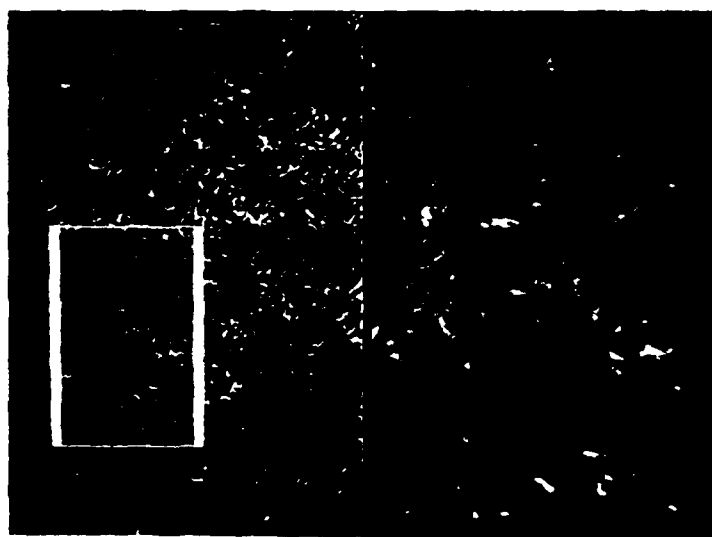


FIGURE 18: Rayperm[®] pore structure after 14 days storage in BrF₃.
~600/1800X

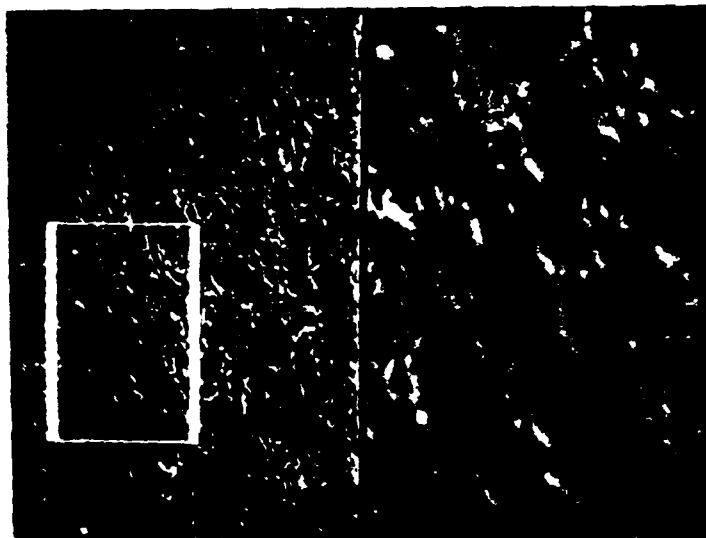


FIGURE 19: Rayperm® pore structure after 30 days storage in BrF_3 .
~600/1800X

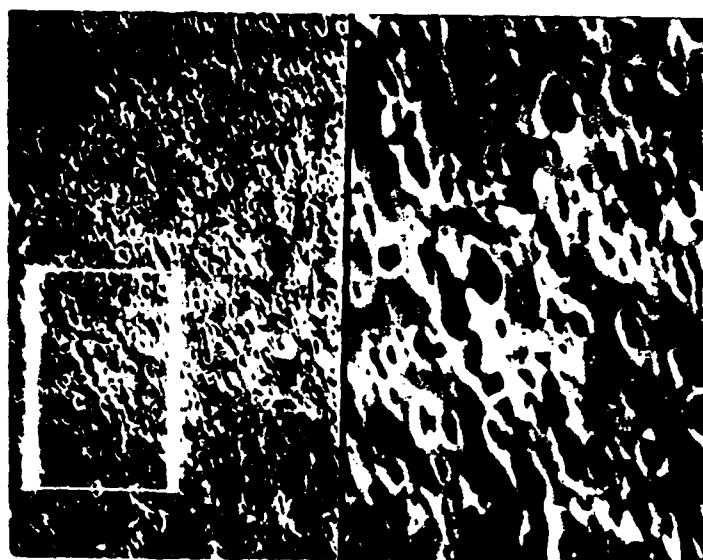


FIGURE 20: Rayperm® pore structure after 180 days storage in BrF_3 .
~600/1800X

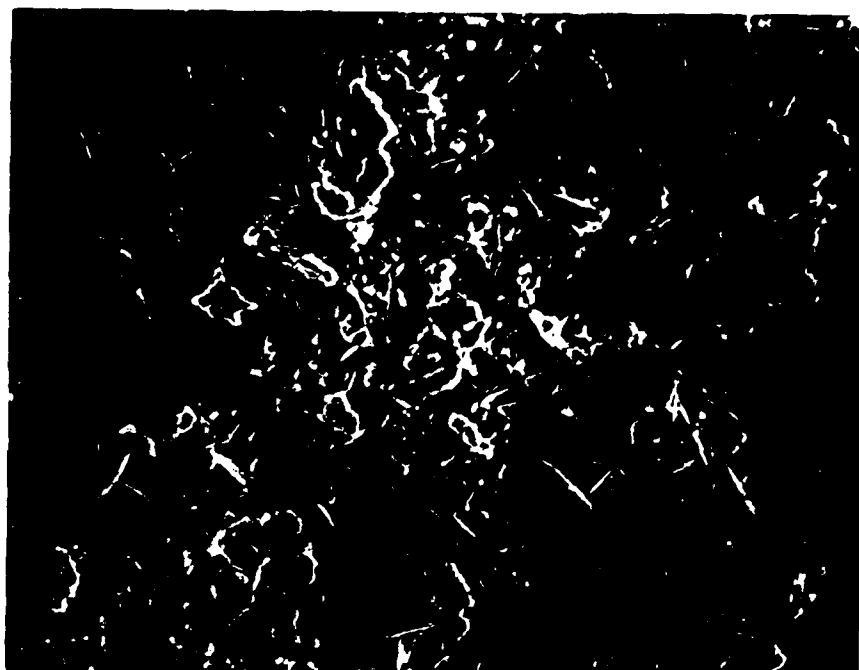
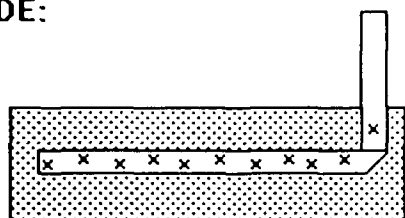


FIGURE 21: Lithium surface after 90 days storage. ~600X

BROMINE TRIFLUORIDE PROTOTYPE CELL COMPONENT SPECIFICATIONS (1/2 AA)

ANODE:



Material:

Lithium

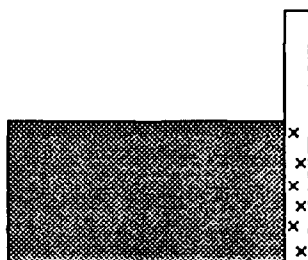
Dimensions:

0.668" X 2.25" X 0.033"

Weight with lead:

0.81 grams

CATHODE:



Material:

Teflon-bound carbon black on ferritic stainless steel expanded metal

Dimensions:

0.750" X 1.50" X 0.032"

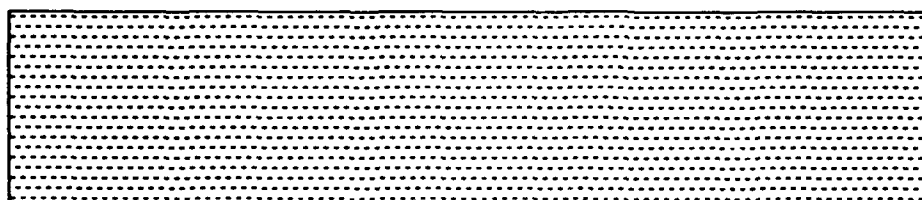
Surface area:

2.25 sq. in. (14.5 sq. cm.)

Weight with lead:

0.65 grams

INNER SEPARATOR:



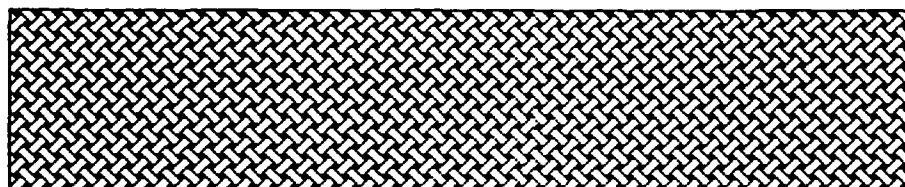
Material:

Microporous Tefzel film

Dimensions:

0.875" X 5.00" X 0.002"

OUTER SEPARATOR:



Material:

Woven Tefzel fabric

Dimensions:

0.875" X 5.00" X 0.007"

DIFFUSER PLATE:



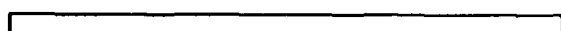
Material:

Woven Tefzel fabric

Dimensions:

0.55"D X 0.007"

ELECTRODE LEADS:



Material:

Ferritic stainless steel

Dimensions:

0.125" X 0.005" X 3.0"

FIGURE 22

SCHEMATIC OF CELL FILLING APPARATUS
FOR BrF_3 PROTOTYPE CELL

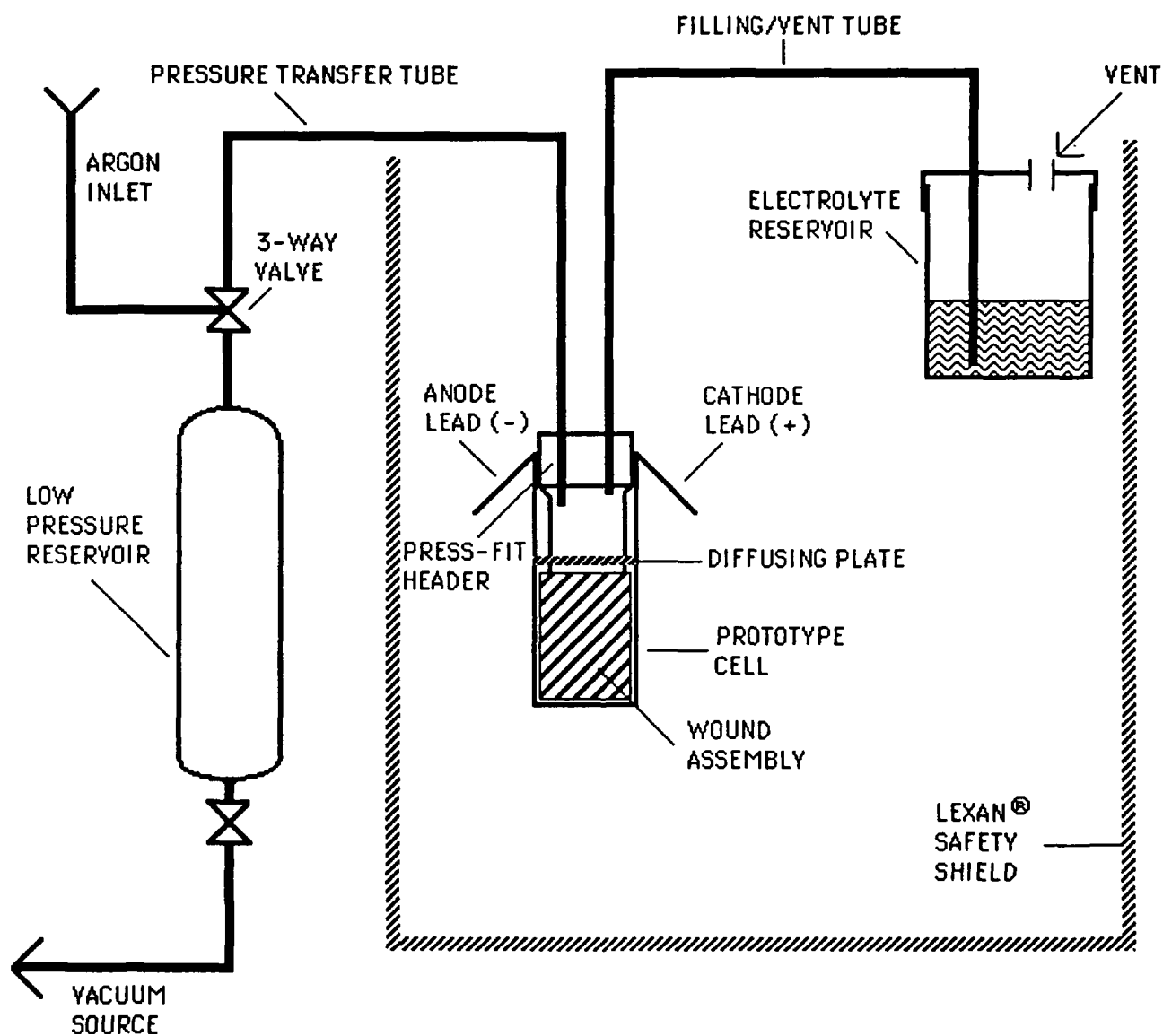
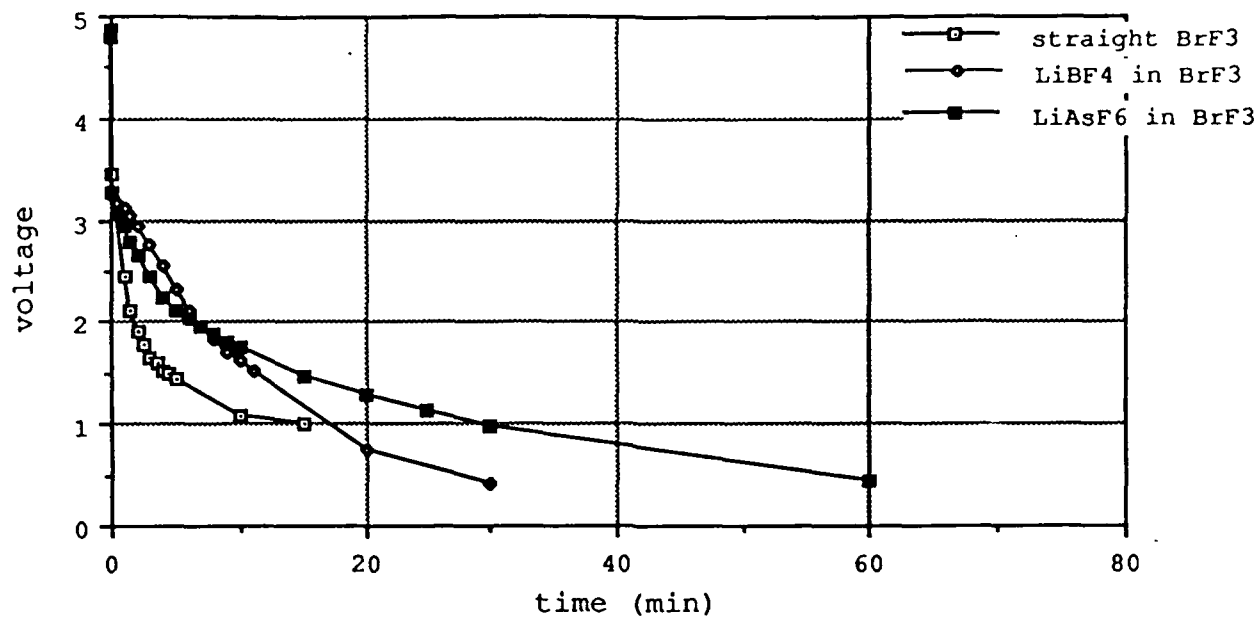
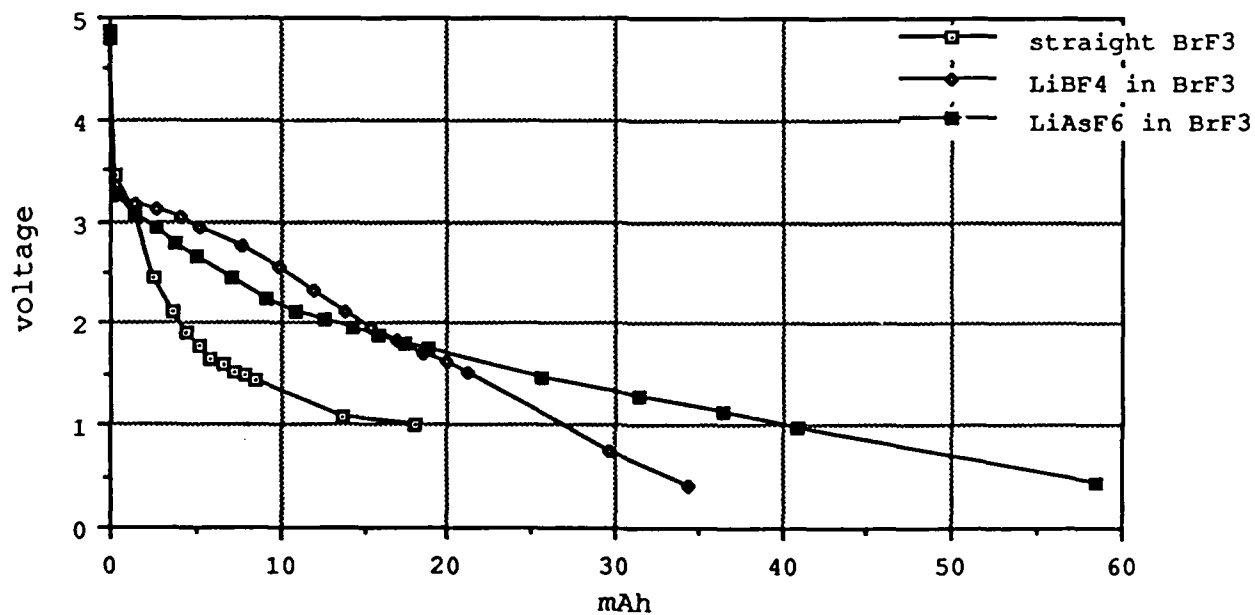


FIGURE 23



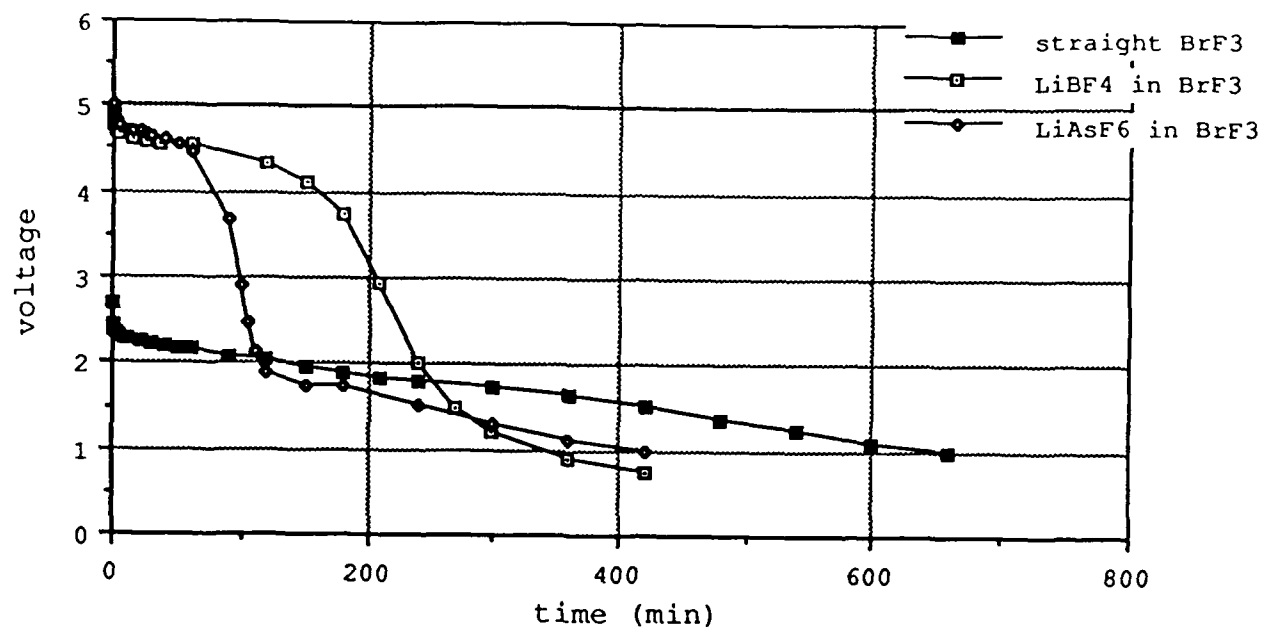
Li/BrF3 1/2AA test cell data on 20Ω discharge.

FIGURE 24



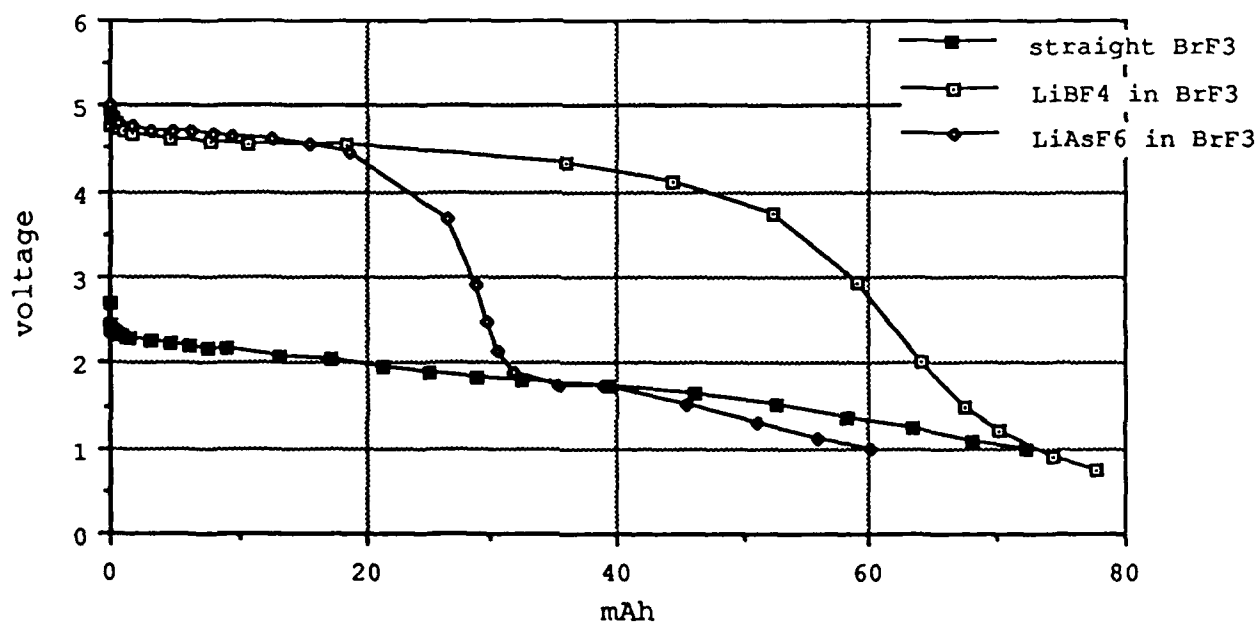
Li/BrF3 1/2AA test cell data under 20Ω discharge.

FIGURE 25



Li/BrF3 1/2AA test cell data on 250Ω discharge.

FIGURE 26



Li/BrF3 1/2AA test cell data on 250Ω discharge.

FIGURE 27